ISOTHERMAL TRANSFORMATION OF DYNAMIC DSC CURVES FOR THERMOSETTING POLYMERS IN CURING KINETICS ANALYSIS

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To predict the isothermal course of a reaction from the dynamic DSC curves, the application of isothermal DSC curve transformation has been proposed. To perform such a transformation, it is sufficient only to determine the effective activation energy. To transform integral dynamic curves, \( a(T) \), into isothermal ones, \( a(t) \), a better equation has been derived and its validity has been demonstrated on the example of two typical thermosetting systems. In addition, it has been shown that the transformation of differential curves, \( \frac{dt}{dt} (T) \), into isothermal ones \( \frac{dt}{dt} (\alpha) \), readily allows determination of the kinetic function and rate constants. The procedure used to obtain information on the curing kinetics for thermosetting resins is characterized by simplicity and reliability and can work at \( E = E(\alpha) \).

To describe reactions occurring in an isothermal DSC process, the equation to be used is as follows:

\[
\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) \cdot f(\alpha)
\]

(1)

while in a dynamic DSC process it is as follows:

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) \cdot f(\alpha)
\]

(2)

where \( \alpha \) is the fractional conversion, \( \alpha = \frac{\Delta H}{\Delta H_0} \) where \( \Delta H \) and \( \Delta H_0 \) are the partial and total heat values, respectively, \( t \) is the time, \( A \) is the pre-exponen-
tional factor, $E$ is the apparent activation energy, $R$ is the universal gas constant, $T$ is the absolute temperature, and $f(\alpha)$ is some function of the fractional conversion. It is often assumed that $f(\alpha) = (1-\alpha)^n$, where $n$ is the reaction order.

A great number of methods are available to determine the kinetic parameters of a reaction from dynamic DTA-DSC and TG curves, but it still remains a problem to obtain reliable values of these parameters. Certain authors are of the opinion that it is impossible in principle to determine reliable kinetic parameters from dynamic TG and DTA-DSC data [1].

It is not surprising that an increasing number of papers are being published where kinetic parameters are obtained from the results of an isothermal experiment [2-5], and all the leading firms (Perkin-Elmer, Du Pont, MOM) therefore provide their instruments with the facilities to perform such an experiment. However, it is not always possible to carry out the experiment.

The main hindrance is the loss of information on the process outset during the introduction of the isothermal mode. Higher heating rates will not solve the problem either. On rapid heating, thermosetting resins may swell; consequently, DSC curves can not be reproduced and, moreover, instrument failure may result. In many cases, therefore, the dynamic experiment remains preferable.

Equivalent conversion methods have been introduced by Ozawa, Flynn et al., Reich et al., and Friedman [6-9] for the calculation of $E$ values as reliable as those obtained from the results of the isothermal experiment [10].

Generally, it is a more difficult task to determine other kinetic parameters, as one must often find not only the reaction order, but also the function $f(\alpha) \neq (1-\alpha)^n$. Without $f(\alpha)$, the pre-exponential factor can not be determined. The well-known equations proposed by Horowitz and Metzger, and Kissinger et al. [11] often yield very approximate and even inappropriate data. It is probably due to this fact that most papers concerned with DSC data-based reaction kinetics often determine only $E$, less often $n$ and seldom $f(\alpha)$.

Recently, some interesting studies have been published, for example [12], in which all kinetic parameters are determined from one curve, even for a multi-stage process. On the other hand, there are no papers where the kinetic parameters derived from the dynamic DSC data for the curing of thermosetting polymers are then used to predict the course of the reaction in the isothermal mode.